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SPECTRAL CHARACTERISTICS OF RADIATION REFLECTED DIFFUSELY BY THE SURFACE OF A CERAMIC TILE

K. Yu. Frolenkov,^{1,3} T. N. Balk,¹ G. S. Parshin,² and O. V. Glazkov²

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The spectral characteristics of radiation diffusely reflected by the surface of a ceramic tile under continuous and pulsed irradiation are compared. The effect of UV radiation on experimental samples is studied. It is shown that the phenomenon of triplet absorption resulting in visible-range phosphorescence is characteristic for ceramic glaze irradiated with a flash lamp. However, the effect of UV radiation on glaze is the appearance of radiation color centers in the glassy network which absorb visible light. All this gives rise to a discrepancy between the results of instrument and visual assessment of the color of a ceramic tile.

Key words: ceramic tile, glaze, frit, color, colorimetry, spectrum, triplet absorption, radiation color centers.

Color plays an extremely important role in today's world. Color appears because of a body's ability to absorb selectively part of the light rays from the total light flux in the visible region of the electromagnetic spectrum and scatter the remaining radiation into the surrounding environment. The color tone perceived is due to the fact that the energy of a definite range of wavelengths predominates and to the sensitivity of the human eye to brightness. Especially important are the facts that color is a subjective phenomenon and depends on the observed [1].

Color reproduction is one of the most difficult problems today in the production of ceramics. Instrument methods for determining color are almost never used in printing on ceramic. The colorimetric characteristics of a tile are checked visually by comparing with standard samples when the finished product on a conveyor is sorted. This method of checking is subjective and depends on an entire range of factors involved in color perception (thresholds of perception of color brightness, color tone, color saturation; room illumination; surrounding color background; and, so on).

The adoption of instrument methods for checking the colorimetric characteristics of ceramic tiles is being held back by the considerable discrepancies between the results of physical measurements and the perceptions of color by people [2]. Indeed, according to [3] the diversity of color perceptions arising for objects under real observational conditions

is always richer than the colorimetric color diversity. Indeed, the quantitative expression of subjective attributes of light is not unique, since it depends on the differences between the concrete conditions under which objects are observed and the standard colorimetric conditions. Specifically, depending on intensity the perception of color can be different even for radiation fluxes with the same spectral composition [3].

However, instrument methods for monitoring the colorimetric characteristics of objects do not require much time, are highly reliable, and yield reproducible results. In addition, the results obtained using instrument methods differ less between each other than the results obtained by visual evaluation [1].

Possible reasons for the disparities between the visual and instrumental evaluations of the color of ceramic tiles are polarization, interference, reflection of light at an interface separating phases, as well as luminescence of ceramic glaze. An additional difficulty is the high sensitivity of visual system of humans to color variations, which is no worse than that of the best instruments, even though the sensitivity of the human eye to color varies very strongly with wavelength [1, 3, 4]. Therefore, the visual evaluation of color depends not only on the spectral distribution of the radiation flux but also on the sensitivity of the human eye as well as on the source of the light in which an object is observed. Color is a sensation arising in the human brain, and it cannot be measured in this form [1]. Nonetheless, the physical parameters which give rise to this perception can be measured.

The object of the present work is to determine the possible reasons for the disparity between instrument and visual

¹ Orel State Technical University (OrelGTU), Orel, Russia.

² Orel State Institute of Economics and Trade (OrelGIÉT), Orel, Russia.

³ E-mail: lara@ostu.ru.

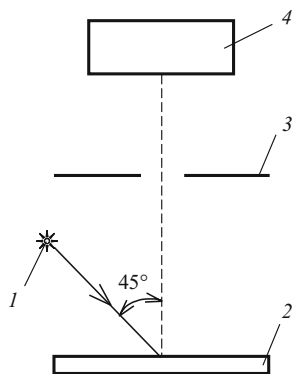


Fig. 1. Scheme for detecting spectral characteristics of radiation diffusely scattered by the surface of a ceramic tile: 1) light source; 2) experimental sample or standard; 3) aperture stop; 4) FÉU-110 photomultiplier.

assessments of color by investigating the spectral characteristics of radiation diffusely reflected by the surface of a ceramic tile as well as to study the effect of UV radiation on experimental samples, specifically, the natural phosphorescence of ceramic glaze and the formation of radiation color centers in it.

Samples of a glazed ceramic tile fabricated at the "Velor" JSC (Orel) were investigated. The glazing was done by the slit method. The glaze was prepared using a semitransparent aluminoborosilicate frit ($\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO} - \text{Fe}_2\text{O}_3 - \text{ZrO}_2 - \text{Na}_2\text{O} - \text{K}_2\text{O}$) produced by "Velor" JSC and ceramic paint produced by the Voronezh Works which produces glazed earthenware. For the present study, eight samples of ceramic tile with the following color range were made: No. 1 — orange; No. 2 — light-green; No. 3 — violet; No. 4. — yellow; No. 5 — dark red; No. 6 — turquoise; No. 7 — dark-green; No. 8 — red.

The spectral coefficients of diffuse reflection of the samples in the wavelength range 380 – 720 nm were determined on a "Pul'sar" spectrophotometer. The operating principle of the instrument is based on the simultaneous measurement of the coefficients of reflection or transmission at twenty four fixed wavelengths in the visible region of the spectrum for a single flash of a flash lamp followed by mathematical analysis of the measurements using a program-technical system. The measurements were performed without taking account of the specular component.

Unfortunately, instruments in which flash lamps are used can give an instrument assessment of color, specifically, white, which is at variance with visual assessment [1]. This is due to a phenomenon called triplet absorption, which is due to the intensity of the light pulse. Thommen has investigated the mechanism of triplet absorption. In a number of substances this triplet absorption is very substantial in the visible range.

This problem does not occur in instruments for which a sample is illuminated continuously, since in this case the intensity of the illumination is comparable to that used for visual assessment. In this connection, a method has been developed for determining the diffuse reflection spectrum of the surface of a ceramic tile using an attachment to the SF-45 spectrophotometer to measure the reflection coefficient of

thin-film coatings [5, 6]. The scheme for detecting the spectral characteristics of radiation diffusely reflected by the surface of a ceramic tile is presented in Fig. 1. This scheme was developed on the basis of recommendations presented in [1], according to which a 45/0 geometry is proposed for determining the spectral characteristics of samples exhibiting luminescence. The angular aperture was 2° , which meets the standard conditions for performing observations and illumination (observation of an object from a large distance). In the measurements, the ratio of the intensity of the light reflected from the experimental sample placed in the measuring port to the intensity of the light reflected from an ideal white standard of the same size as the sample placed in the same port. The tray compartment of the SF-46 spectrophotometer, supplemented with a light-proof chamber expanding the over-all volume of the tray division, which is necessary to insert a photomultiplier and obtain the required measurement geometry, was used as the measuring port. Slightly pressed and finely ground MgO , diffusely reflecting more than 90% of the incident light [1, 4], was used as the standard white light. The measurements were performed in the wavelength range 380 – 720 nm with step size 10 nm.

The spectral curves of the diffuse-reflection coefficients \tilde{n} of the experimental samples are shown in Fig. 2. The observed differences of the spectral dependences of the reflection coefficients obtained on the "Pul'sar" spectrophotometer and the SF-46 spectrophotometer attest to the presence in the experimental glazes of triplet states which are excited by light pulses and absorb in the visible wavelength range.

The presence of triplet states should cause phosphorescence in the glaze [1, 7]. According to [8] for UV irradiation of glass with alkali and alkali-earth oxides energy accumulates in the glassy network, and large fraction of this energy is stored in radiative color centers. The destruction of these centers results in recombination afterglow (phosphorescence) in the range from 1.5 to 5.0 eV ($2.48 \times 10^{-7} \leq \lambda \leq 7.99 \times 10^{-7} \text{ m}$). Accordingly, the kinetics and spectral range of phosphorescence of frit used to prepare the experimental glazes were investigated.

The phosphorescence of the frit was recorded on a luminescence measuring setup described in [9, 10]. Slightly pressed, finely ground samples of frit pre-irradiated over three minutes by a PRK-100 mercury lamp were placed in front of the cathode of a photomultiplier (FÉU-110), located in the light-proof chamber of the setup. The UV-light source and the photomultiplier were equipped with special covers-shutters which protected the photocathode of the photomultiplier from illumination during UV irradiation and the after-glow of the mercury lamp during the phosphorescence measurements.

It was found that the experimental frit exhibits quite bright phosphorescence, observed after the sample is irradiated with the mercury lamp. The kinetic curve of the intensity I of the phosphorescence of the sample is shown in Fig. 3. It is evident that the kinetics of the phosphorescence

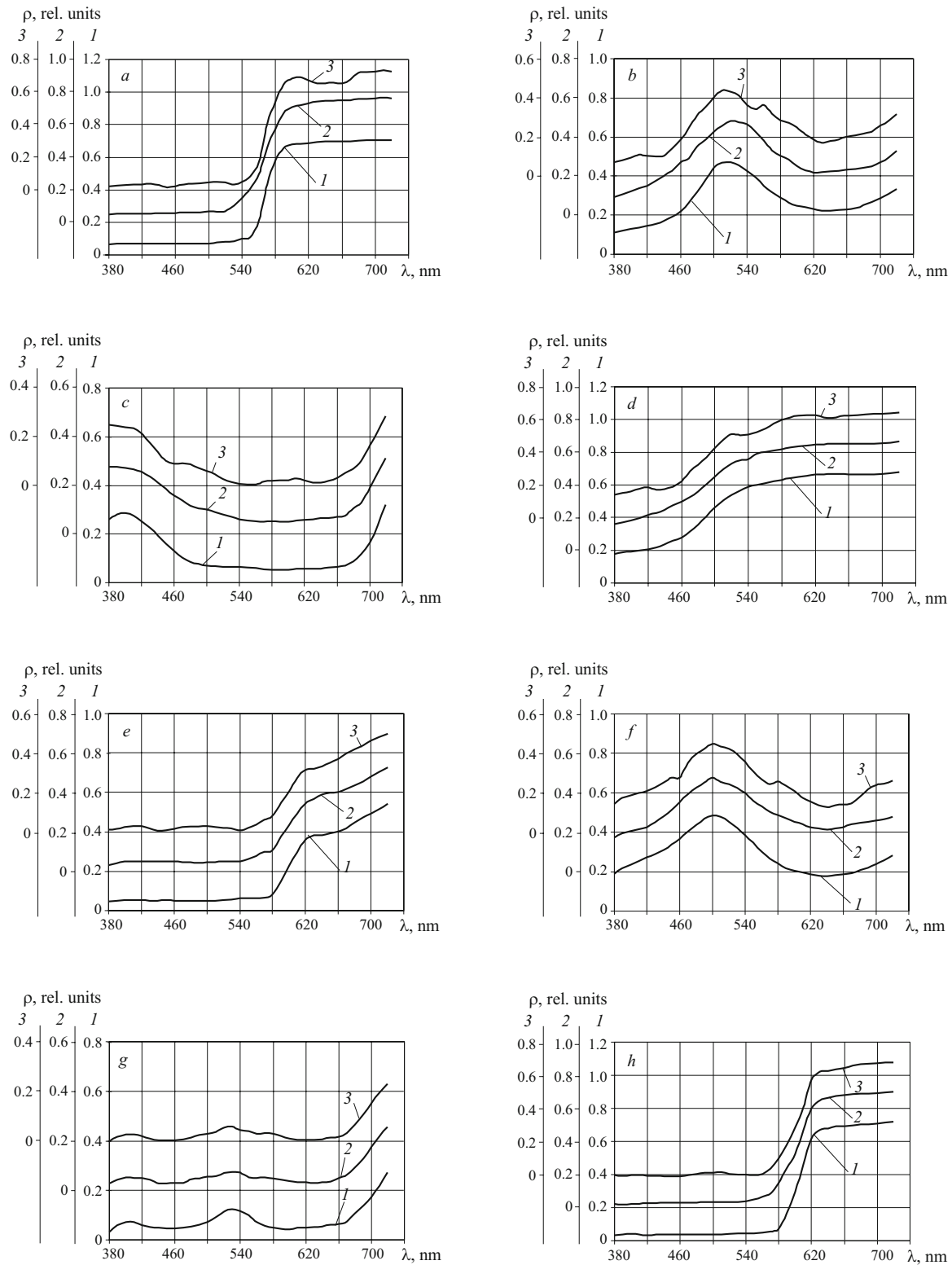


Fig. 2. Comparison of the spectral curves of the diffuse reflection coefficient obtained with the following: 1) Pul'sar spectrometer; 2) SF-46 spectrophotometer without UV pre-irradiation; 3) SF-46 spectrophotometer after UV pre-irradiation; a) sample No. 1; b) sample No. 2; c) sample No. 3; d) sample No. 4; e) sample No. 5; f) sample No. 6; g) sample No. 7; h) sample No. 8.

intensity follows well the Becquerel hyperbolic law, whose phenomenological theory is described in [8].

After UV irradiation of the samples spectral analysis of the light sum was performed by analogy to [8, 11, 12] using

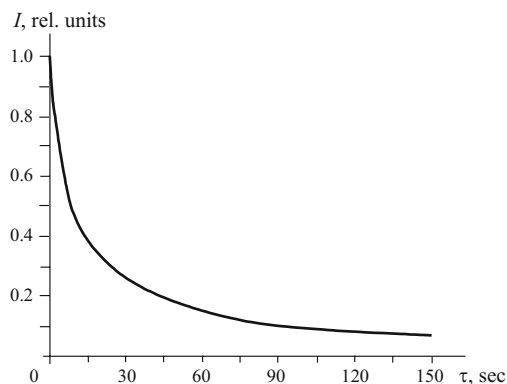


Fig. 3. Kinetics of the intensity of phosphorescence of a frit sample after irradiation by a mercury lamp.

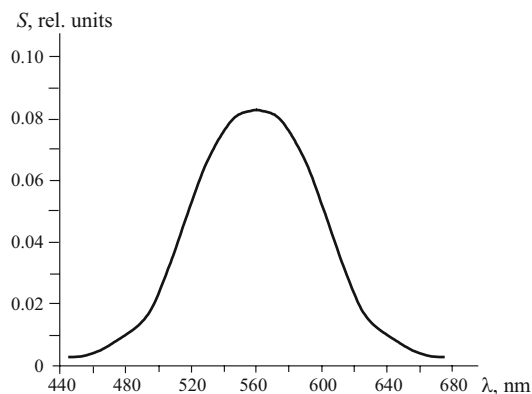


Fig. 4. Spectral curve of the phosphorescence of the experimental frit after UV irradiation by a mercury lamp.

light filters which have a sharp transmission boundary. A set of samples of optical colored glass (GOST 9411–81) was used for this. To prevent any influence of the UV radiation in the measurements light filters were placed between the cover-shutter and the photocathode of the photomultiplier. The ratio S of the light sum of the phosphorescence recorded by the photomultiplier in the presence of light filters to the light sum of the phosphorescence recorded in their absence was determined. Assuming, following [8, 13], the spectrum of the phosphorescence to be bell-shaped the spectral characteristic of the phosphorescence of the experimental frit after UV irradiation by the mercury lamp was determined (Fig. 4).

According to Fig. 4 the phosphorescence is observed in the visible range, the spectral maximum lying in the range 540 – 580 nm. This correlates well with the data presented in [8] on the thermoluminescence of UV pre-irradiated sodium and potassium silicate glasses. Thus the phosphorescence of frit after UV irradiation must occur according to [8] as a result of the activation of electrons or holes, their freeing from traps, and their recombination on radiative color centers.

All this confirms the previously stated supposition on the possibility of distortion of the results of instrument assessment of the color of ceramic samples because of triplet absorption in the case of irradiation by the flash from a flash lamp. In this connection, the effect of UV pre-irradiation of experimental samples on the character of the spectrum of their diffuse reflection was evaluated. The irradiation was performed by a PRK-100 lamp from 3 min. To eliminate any effect on the phosphorescence reflection spectrum the experimental samples were held in the dark at room temperature for 3 days. The diffuse reflection spectrum was obtained using the SG-46 spectrophotometer according the procedure described above.

The measurements are presented in Fig. 2. When the spectral reflection curves of the UV pre-irradiated and unirradiated samples were compared it was found that for the irradiated sample three regions characterized by relatively weak absorption bands can be identified to a first approximation. These are wavelength regions 430 – 460, 520 – 560,

and 600 – 50 nm. Since all experimental glazes contain the same frit the observed absorption bands can be explained, following [8, 13], by the formation on UV irradiation in the glassy network of radiation color centers, i.e. defects which absorb visible-range light. Specifically, according to [8] the absorption band 430 – 460 nm can be interpreted as being due to the formation of [Al] and [B] hole centers, the absorption band 520 – 560 nm can be attributed to the formation of $[Al_{3/2}O^-M^+]$ type hole centers (hole center on a aluminum-oxygen site), and additional optical absorption by micro-segregations of sodium-borate glass, this type of absorption being due to the appearance of electronic centers under UV irradiation, and finally the absorption band 600 – 650 nm due to the formation of electronic E'_1 centers (for example, an electron capture on an oxygen vacancy) as well as an absorption band due to no-bridge oxygen.

The following conclusions can be drawn from the results obtained:

- triplet absorption resulting in visible-range phosphorescence is characteristic for the experimental samples of ceramic glaze irradiated with a flash lamp;
- radiation color centers absorbing visible light arise in the glassy network when the experimental samples are irradiated with UV radiation;
- this cannot but lead to discrepancies between the results of instrument and visual (especially in natural light) assessments of the color of a ceramic tile.

In summary, when measurements of the color of ceramic glazes are performed on the basis of the spectral reflection curves it must be kept in mind that any instrument employing monochromatic radiation and a polychromatic detector will refer the entire observed response to the wavelength of the monochromatic radiation. On the other hand, because of triplet absorption, instruments which employ flash lamps give color assessments which do not correspond to visual assessment. The solution of the problem is to use a double monochromator — the classical method of measuring the color of materials exhibiting luminescence.

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